Determining the strengths of hydrogen bonds in solid-state ammonia and urea: Insight from periodic DFT calculations

Manuscript received: 23/09/2002; Article published: 22/01/2003

Determining the Strengths of Hydrogen Bonds in Solid-State Ammonia and Urea: Insight from Periodic DFT Calculations**

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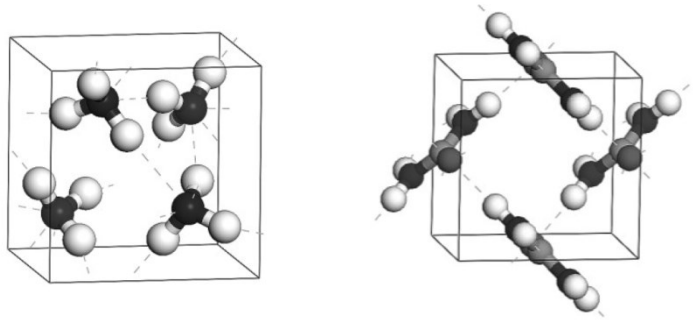
[**]C.A.M. gratefully acknowledges The Royal Society for the award of a University Research Fellowship and the University of Edinburgh (School of Chemistry) for financial support. M.M.S. is grateful to the University of Edinburgh (Schools of Chemistry and Physics) for the award of a Research Studentship. Both authors thank Dr. R. O. Gould, Prof. D. W. H. Rankin (School of Chemistry, University of Edinburgh) and Dr. W. G. Marshall (Rutherford Appleton Laboratories) for helpful discussions on hydrogen bonding during the preparation of this manuscript.

Supporting information:
Supporting information for this article is available on the WWW under http://www.wiley-vch.de/contents/jc_2111/2003/f4443_s.pdf or from the author.

Graphical abstract:



Keywords:
ammonia; Car–Parrinello; plane-wave density functional calculations; hydrogen bonds; urea

Abstract

Plane-wave density functional theory has been applied to determine the strengths of hydrogen bonds in the phase I crystal structures of ammonia and urea. For ammonia, each component of the trifurcated hydrogen bond has been found to be almost as strong as a standard N-H···N interaction, and for urea the strengths of the two different N-H···O interactions have been determined by a quantum mechanical technique for the first time.

Main text

Estimating the energy of hydrogen bonds1 in the solid state by experimental means is a complex business, and often all the information a chemist would desire cannot be directly measured. For example, in order to identify the principal driving forces responsible for crystal packing, it would be necessary to determine the strengths of all of the different hydrogen bonds present, rather than an average value that may be obtained on the basis of thermochemical measurements. In recent years chemists have increasingly turned to computational methods to explore intermolecular interactions. However, whilst the phenomenon to be modelled frequently arises due to the periodic nature of the crystal lattice, the nature of the calculation often employed [i.e., ab initio molecular orbital (MO) theory] is only, in effect, relevant to studying isolated systems. Thus a dimer, or perhaps a small cluster, is constructed to model a property of matter that occurs over a three-dimensional network. Without periodic boundary conditions, the dangling valency sites and absence of crystal packing forces may result in an optimised structure significantly different from the solid-state structure it was designed to imitate. Hydrogen bonding has also been described as a nonadditive effect;1 that is, the strength of a network of *N* interconnected hydrogen bonds is not just the sum of*N* isolated bonds. In these cases, it is therefore undesirable to split up the network into individual hydrogen bonds and calculate the energy of each one. Moreover, in the solid state, the lone pair on the electron-donor atom (e.g. nitrogen or oxygen) will often interact with two or even three hydrogen (acceptor) atoms, creating bi- or trifurcated hydrogen bonds,1 whereas the optimised models of the nonperiodic dimer complexes used to mimic the solid-state structure may contain only standard hydrogen bonds, in which the donor interacts with only one acceptor.

Aside from the validity of the models used, a further problem may arise from the use of localised basis sets to estimate binding energies. The results obtained may suffer from basis-set-superposition error (BSSE), which can result in an overestimation of binding energies and must be corrected for. Attempts to account for this effect mostly employ the Counterpoise method,2 but some studies in the literature point to this correction as being strongly dependent on the quality of the basis sets used.3

For all these reasons, the task of calculating the properties of hydrogen bonds in the solid state really needs a style of modelling in which periodicity is inherent in the calculation. One such method is Car–Parrinello or

plane-wave density functional theory,4 which can simulate a repeating model such as a crystallographic unit cell. The atomic positions and lattice vectors can all be varied to minimise the lattice energy, atomic forces and unit cell stress. As the valence-electron treatment is delocalised in this style of calculation, any calculated binding energies will be free from BSSE. Moreover, this style of computational modelling is very versatile; once convergence with respect to the basis set has been achieved, the dimensions of the periodic cell used can take any size or shape. Taking the crystal structure coordinates as the starting point, the unit cell parameters and atomic positions are optimised alternately until convergence is met. Removing all but one molecule from the periodic cell, and stretching the cell vectors (so that the remaining molecule cannot "see" its counterparts in neighbouring cells), will allow the energy of one (effectively gas-phase) molecule to be determined. As the same basis set and level of theory are employed in both cases, comparing the absolute energies obtained is valid. This therefore allows the determination of lattice or sublimation energies (after correcting for atom relaxation in the gas phase and zero-point-energy effects); this in turn allows the strengths of intermolecular interactions to be inferred.

The main purpose of this paper is to demonstrate the application of plane-wave DFT to the determination of the lattice energies and strengths of hydrogen bonds in the solid-state structures of ammonia and urea. Both compounds have previously been subjected to extensive calculations by ab initio MO theory by using dimer models to deduce the strengths of intermolecular interactions in the gas phase. This paper begins with a brief summary of what is currently available in the literature, before discussing the results obtained for the ammonia and urea test cases.

Hydrogen bonds—ammonia

Despite the difficulties in determining the strength of the hydrogen bond between molecules of ammonia from experiment, a number of attempts have been made. Most undergraduate textbooks quote the interaction strength as 17.0 kJ mol^{-1},5although no reference is cited as to how this value has been obtained. A very elegant paper by Scheraga et al,6 highlights all the steps necessary to determine the lattice and sublimation energies on the basis of thermodynamic measurements. Their value for the sublimation energy, 29.0(42) kJ mol^{-1}, gives a hydrogen bond energy of 9.7(14) kJ mol^{-1}, assuming that all the interaction energy in the crystal lattice is due to hydrogen bonding and that each ammonia molecule is involved in six hydrogen bonds (i.e., bond order 3). Another experimental (microwave) study focuses on the gas-phase ammonia dimer and places an upper boundary of 11.7 kJ mol^{-1} on the hydrogen bond dissociation energy.7a It should be noted that the interaction present in the ammonia dimer (i.e., gas phase)7a,7b is very different from that which occurs in the condensed state.8a,8b In the dimer model a standard hydrogen bond occurs in which the nitrogen lone pair donates electrons to one neighbouring hydrogen atom. In the solid state the lone pair donates electrons to three

neighbouring hydrogen atoms (i.e., a trifurcated bond, see Figure 1). In any case, regardless of whether the measurements relate to the gas or solid phase, both experimental results are at odds with the textbook value.

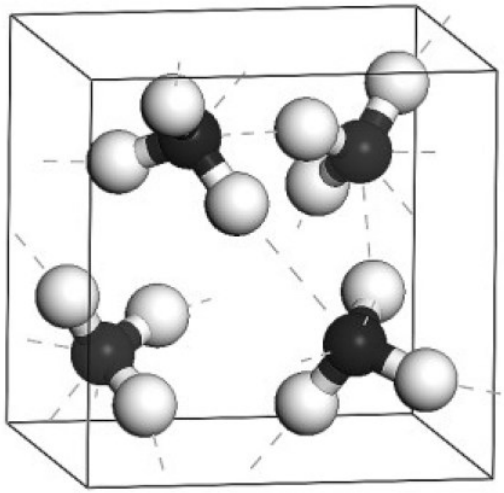


Figure 1. The phase I crystal structure of ammonia.

A number of different dimer structures have been reported on the basis of ab initio molecular-orbital calculations. Some reports refer to a classical linear dimer structure,9a,9b while other calculations refer to a nonlinear dimer9c or cyclic structure (with two hydrogen bonds per dimer)9b as being almost degenerate in energy. Subsequent variations in the reported hydrogen bond strengths range from 6.6 to 13.1 kJ mol^{-1}.9 Microwave studies,7a,7b favour the nonlinear dimer structure on the basis of measured dipole moments. From this literature survey it is clear that the potential-energy surface for the ammonia dimer system is very complicated, and leaves the determination of the intermolecular interaction energy in the solid state as an interesting challenge.

Hydrogen bonds—urea

There are two different N-H···O interactions present in the phase I crystal structure of urea;10 one links planar molecules together to form chains, whilst the other occurs between perpendicular chains that run in opposite directions. The hydrogen bond order for each urea molecule is four (Figure 2).

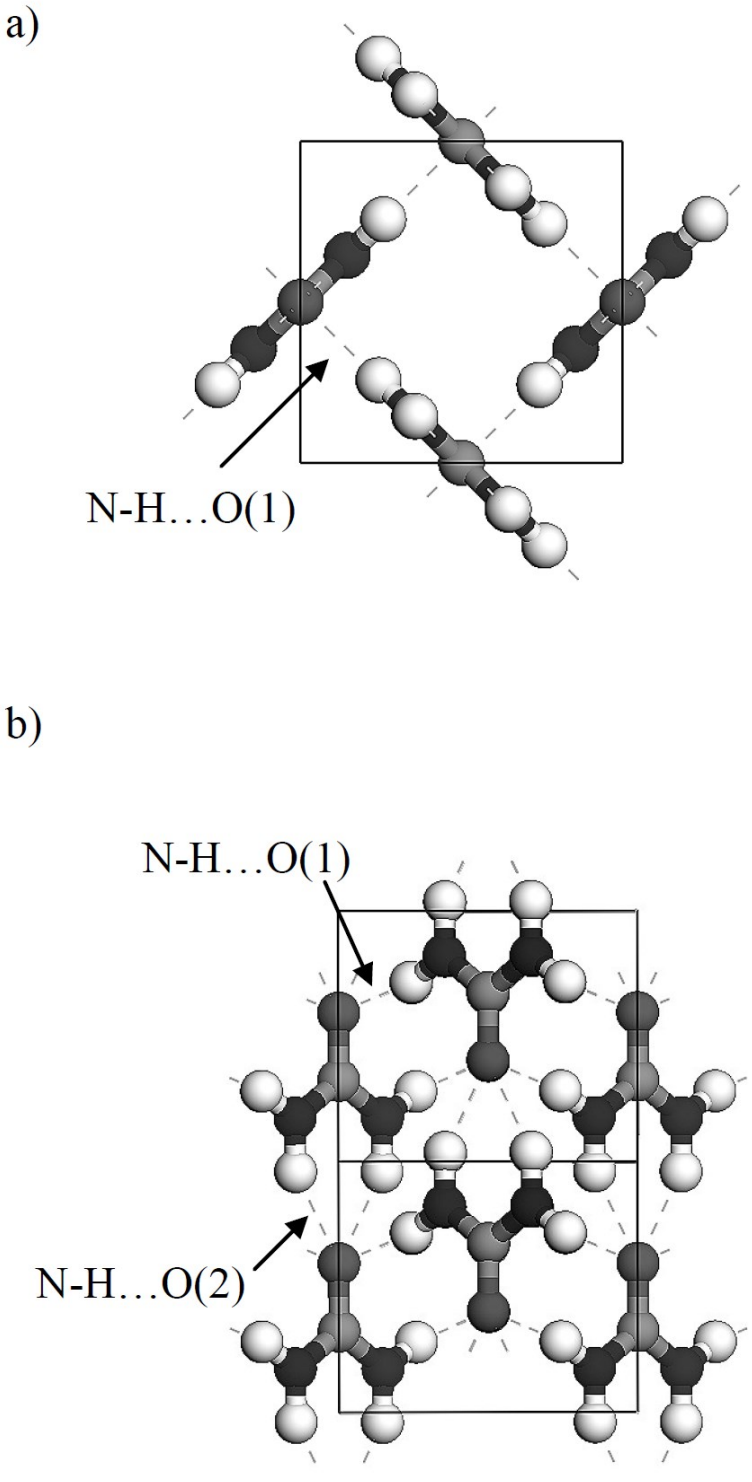


Figure 2. The phase I crystal structure of urea, showing a) N-H···O(1) and b) N-H···O(2) hydrogen bonding interactions.

Two computational studies reported in the literature model properties of hydrogen bonds in the solid state.11–12 Both employ the Hartree–Fock Linear Combination of Atomic Orbitals (HF-LCAO) approach for periodic systems as implemented in the CRYSTAL suite of software.13 Using a double-zeta quality basis set Dovesi et al.11 report an average hydrogen bond energy of 18.2 kJ mol^{-1} after Counterpoise correction (albeit with no mention of zero-point energy correction, or optimisation of the crystal structure coordinates or cell parameters); this compares well with the experimental value (21.9 kJ mol^{-1}) obtained from the sublimation energy.14 Gatti et al.12 report a study of the topology of the electron density using Bader's Atoms in Molecules (AIM) method,15 rationalising the ability of the carbonyl oxygen to form two bonds in the gas phase and four in the solid. They predict that N-H···O(1) should be shorter (and stronger) than N-H···O(2) (Figure 2). Another experimental/theoretical report (based on a modified atom–atom approximation scheme, parameterised by using experimental X-ray and theoretical Hartree–Fock structure amplitudes) has assigned values of 15.7 kJ mol^{-1} and 28.2 kJ mol^{-1} to N-H···O(1) and N-H···O(2), respectively.16 Their average hydrogen bond strength, at 21.9 kJ mol^{-1}, is a perfect match with experiment, but the ordering of the strengths of the two interactions is the reverse of that predicted by Gatti.

There are several reports in the literature of ab initio molecular-orbital calculations for the dimer species [Figure 3a], which to a first approximation could be used to model the interactions that occur between molecules in a chain in the crystal lattice [i.e., N-H···O(2)]. Reported values for the strength of this hydrogen bond are about 17 kJ mol^{-1},17–18 falling to 15 kJ mol^{-1} after Counterpoise correction. Exemplary work by Dannenberg et al.18 shows that as this dimer unit is extended to form an infinite one-dimensional chain, the strength of the intermolecular interaction increases by almost 10 kJ mol^{-1}; this illustrates nicely the principle of bond nonadditivity due to resonance effects. There are no publications reported on dimer models appropriate to model the interaction that occurs between perpendicular chains in the crystal lattice [i.e. N-H···O (1)]. It is therefore our objective to demonstrate the use of plane-wave DFT to determine the strengths of both interactions in the proper periodic framework of the phase I crystal structure of urea, and thus determine which of the two interactions is stronger.

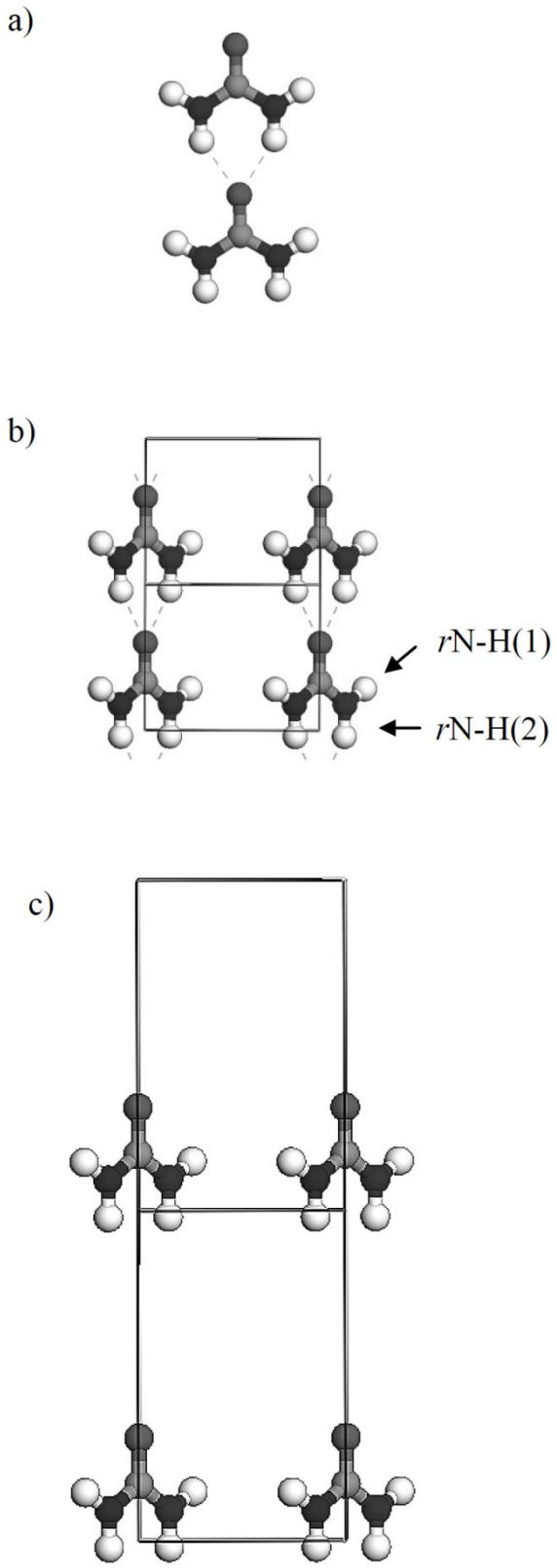


Figure 3. Urea models: a) Isolated molecule dimer model (C_{2v}) used in ab initio MO calculations, b) model with one stack of urea molecules removed [destroying contact N-H···O(1)] and c) model stretched along lattice vector "*c*" [destroying contact N-H···O(2)].

Results and Discussion

Ammonia

Our calculated structure (geometry and lattice vectors) matches very closely with the experimental results of Hewat et al.8a for ND_3 at 2 K (neutron diffraction) (Table 1), and also with the most recent work by Boese et al. on NH_3 at 160 K (X-ray diffraction).8b The volumes of the two experimental cells differ by almost 5 %, but this can be entirely attributed to thermal expansion, as the same authors report an almost identical cell volume for ND_3 at 180 K.8a

Table 1. Comparison between the experimental and calculated structures of solid ammonia.

	Experimental		**Calculated**		
Parameters	**Solid[a]**	**Gas[b]**	**Solid**	**Supercell**	**Supercell**
				(not relaxed)	**(relaxed)**
Lattice [Å, °]					
a=*b*=*c*	5.048	–	5.156	8.000	8.000
α, β, γ	90	–	90	90	90
Z	4	–	4	1	1
Volume [Å^3]	128.6	–	137.0	512.0	512.0
Space/point group	$P2_13$	–	$P2_13$	C_{3v}	C_{3v}
Geometry [Å, °]					
*r*N-H	1.061(5)	1.008(4)	1.029	1.029	1.022
*r*N···H	2.357(2)	–	2.329	–	–
*r*N···H	3.325(2)	–	3.322	–	–
≦H-N-H	107.5(2)	107.4(2)	107.8	107.8	108.0
≦N-H···N	160.0(2)	–	161.8	–	–
Energy					
Total energy [eV]	–	–	−1286.342489	−321.218044	−321.220686
Lattice energy [kJ mol^{-1}]	36(4)	–	–	35.4	–
Sublimation energy [kJ mol^{-1}]	29(4)[c]	–	–	–	27.9
H-bond strength [kJ mol^{-1}][d]	9.6(14)	–	–	–	

[a] From ref. 8a. [b] From ref. 19. [c] From ref. 6. [d] Estimated from ΔH_{sub} (i.e., $\Delta H_{sub}/3$).

The calculated unit-cell volume is within 6.5 % of that determined by Hewat and 1.5 % of the volume determined experimentally by Boese. The very close match with Boese's value should not be treated as an

indication of the accuracy of the calculation, as DFT calculations with generalised gradient approximation (GGA) functionals always tend to simulate cells with slightly larger volumes. Indeed, comparison with the ND_3 molecular geometry at 2 K is more relevant in this case, as our calculation refers to the equilibrium structure (i.e., 0 K), and any isotope effect on geometry will be negligible at such a low temperature. In addition, a neutron-diffraction study, measuring internuclear distances (rather than the distances between areas of high electron density as with X-ray diffraction) is clearly more relevant for a direct comparison with theory. For these reasons, the experimental values of Hewat, rather than those of Boese, are provided for comparison with theory in Table 1.

In general, our calculated molecular geometry is in good agreement with the experimental structure, with the N—H bond length reproduced to within 0.03 Å and the two N···H separations to within 0.03 and 0.003 Å of the experimental values. The two angles, H-N-H and N-H···N, are also in good agreement with experiment (within 0.3° and 1.8°, respectively). Finally, the N···N separation in our calculation models the experimental bond distance to within 1 %.

The molecular geometry of NH_3, calculated by using the supercell (i.e., isolated molecule) approach and plane wave basis set, is also very close to the experimental (gas phase) geometry,19 and is no less accurate than the most sophisticated localised basis-set calculation. Although for a true gas-phase calculation the localised basis set approach is clearly the more appropriate method, our calculations nevertheless demonstrate the strength of the periodic style of calculation to reproduce gas-phase geometries. The H-N-H bond angle, at 108.0°, is within the range obtained by most ab initio MO calculations (104.2–108.3°).8b

The results from our calculations show that the molecular geometry of ammonia changes very little upon condensing from the gas to the solid phase, with ≦H-N-H decreasing by 0.2° and *r*N—H increasing by just 0.007 Å. From experiment, the evidence for structural change is ambiguous: Hewat8a and Olovsson20 found an increase in the N—H bond length [by 0.05 Å (neutron diffraction, 2 K) and 0.11 Å (X-ray diffraction, 170 K)] and very small changes in the H-N-H angle (of +0.1° and −0.4°, respectively), but Reed21 and Boese8b report *r*N—H shortening [by 0.003 Å (neutron diffraction, 77 K) and 0.17 Å (X-ray diffraction, 160 K)] and much larger changes for ≦H-N-H (+1.6° and +3.0°, respectively), as compared with the gas-phase microwave structure.19 What is clear, however, is that any change in molecular geometry due to a change in phase is small, and therefore any close analysis for systematic differences in experimental data obtained by using different methods at varying temperatures is not a straightforward exercise. On the other hand, the calculations we have performed on the crystal lattice and supercell models were carried out as much as possible under the same computational constraints, and therefore perhaps allow for a more meaningful comparison to be made.

The lattice energy for the phase I structure of ammonia is calculated as the energy difference between a single, fully optimised molecule in the crystal environment (i.e., unit cell energy/*Z*, here *Z*=4) and a single-point energy calculation of one molecule (in the crystal structure molecular geometry) in the 8×8×8 $Å^3$ supercell.

The value obtained, 35.4 kJ mol^{-1}, is a very close match with the experimental value, 36(4) kJ mol^{-1};6 this bears testament to the quality of the calculations performed. To obtain the sublimation energy from the lattice energy (and thus deduce the strength of hydrogen bonds in the crystal structure) two further steps are required: i) relax the isolated molecule (i.e., obtain the gas-phase geometry), and ii) correct the crystal lattice energy for the effects of intermolecular zero-point vibrational energy (i.e., assuming corrections for the intramolecular vibrations in the solid and gas phase to be the same, therefore cancelling each other out). The first step is straightforward, but for the second the software package we used does not currently support the calculations required to obtain the correction factor.4 We have therefore taken the experimental value for the approximate zero-point vibration correction as reported by Scheraga et al. (7.33 kJ mol^{-1}).6 Our calculated value for the sublimation energy will therefore also closely resemble the experimental value (27.9 vs. 29(4) kJ mol^{-1}).

We note in passing that Eucken et al. have also reported a value for the sublimation energy of ammonia.22 At 31.4 kJ mol^{-1}, it is a little higher than that derived by Scheraga,6 but given that their value was obtained at 169 K, not 0 K (as with Scheraga and our calculations), when the necessary enthalpy corrections to cool the solid and gas phases to 0 K are included we would expect their number to fall by 2–3 kJ mol^{-1}.6

Assuming that the interaction energy is due solely to hydrogen bonding,23 and that each ammonia molecule in the crystal lattice is a three-bond donor and acceptor, our calculated sublimation energy assigns a value of 9.3 kJ mol^{-1} per N-H···N interaction. It would therefore appear that the energies of the three components of the trifurcated bond are each almost equivalent to that of a standard N-H···N interaction, that is, the interaction energy per ammonia molecule in the solid state is nearly three times that determined for the gas-phase dimer. From a comparison of the electron-density maps for ammonia in the crystal lattice and supercell (see Supporting Information, Figure 1a and b), it would appear that there is no discernible change in the size or position of the lone pair upon formation of hydrogen bonds. This would perhaps indicate that the nature of the interaction is largely electrostatic, rather than due to a donation of electrons. For completeness, we also offer electron density images of the hydrogen bonds in the crystal lattice (Supporting Information, Figure 1c and d). As far as we are aware this is the first comparative study of standard versus trifurcated hydrogen bond strengths.

Urea

The results obtained from the unit cell and geometry optimisation for the phase I crystal structure of urea (equilibrium structure) are given in Table 2, alongside the experimental structure (neutron diffraction, 12 K) for direct comparison. From this it can be seen that, as with ammonia, the plane-wave DFT calculation slightly overestimates the volume of the unit cell. However, the volume increase is less than 1.5 %, which translates to an increase in unit cell vectors of no more than 0.04 Å for lattice vectors "*a*" and "*b*" (or 0.005 Å for lattice vector "*c*"). The molecular structure is also well reproduced, with *r*C—O and *r*C—N modelled to

within about 0.005 Å of experimental values. The N—H bond lengths are overestimated in the simulation by about 0.015 Å. However, Swaminathan et al.10 note that applying corrections for harmonic thermal motion increases these lengths to about 1.020 Å, which would be in very strong agreement with the calculation. The two hydrogen bond lengths are both modelled to well within 0.01 Å.

Table 2. Comparison between the experimental and calculated structures of solid urea.

Parameters	**Experimental**		**Calculated**		
	Solid[a]	**Gas**[b]	**Solid**	**Supercell**	**Supercell**
				(not relaxed)	**(relaxed)**
Lattice [Å, °]					
a=*b*	5.565	–	5.604	10.0	10.0
c	4.684	–	4.689	10.0	10.0
α, *β*, *γ*	90.0	–	90.0	90.0	90.0
Z	2	–	2	1	1
Volume [Å^3]	145.1	–	147.1	1000.0	1000.0
Space/point group	$P\bar{4}2_1m$	–	$P\bar{4}2_1m$	C_{2v}	C_2
Geometry [Å]					
*r*C-O	1.261(2)	1.221	1.269	1.269	1.229
*r*C-N	1.345(1)	1.378	1.343	1.343	1.367
*r*N-H(1); *r*N-H(2)	1.009(2); 1.005(2)	1.021; 0.998	1.025; 1.024	1.025; 1.024	1.014; 1.014
*r*H···O(1)	1.992(2)	–	1.994	–	–
*r*H···O(2)	2.058(2)	–	2.046	–	–
Energy					
Total energy [eV]	–	–	−2408.699947	−1203.402552	−1203.5071909
Lattice energy [kJ mol^{-1}]	–	–	–	91.4	–
Sublimation energy [kJ mol^{-1}]	87.6(9)[c]	–	–	–	81.3
Average H-bond strength [kJ mol^{-1}][d]	21.9	–	–	–	20.3

[a] From ref. 10. [b] From ref. 24. [c] From ref. 14. [d] Estimated from ΔH_{sub} (i.e., $\Delta H_{sub}/4$).

The molecular structure obtained in the supercell calculation, is also a good match for the experimental (microwave) geometry.24 In particular, care was taken to ensure that the structure fell into the puckered (C_2)

geometry, which has been found by several computational studies to be the global minimum,25 rather than the planar (C_{2v}) local-minimum structure. Considering the geometry itself, the accuracy of the structure returned in the plane-wave DFT calculation is comparable to that obtained from high-level ab initio MO calculations, although the C—N bond is found to be a little bit shorter (by about 0.01 Å).25

The lattice energy for urea has been determined in exactly the same way as for ammonia (i.e., $H_{lattice}=E_{unit\ cell}/Z-E_{supercell}$), although in this case there is no experimental value available in the literature for comparison. Our estimate of the sublimation energy has been obtained by introducing a correction for solid-to-gas molecular structure relaxation, but no correction for zero-point energy has been applied at this time. An experimental value for the sublimation energy is available,14 and at 87.6(9) kJ mol^{-1} it shows our calculated value (81.3 kJ mol^{-1}) to be in approximately the right area.

The calculated sublimation energy allows us to determine the average hydrogen bond strength. As each urea molecule has a hydrogen bond order of four (Figure 2), we calculate the average hydrogen bond strength to be 20.3 kJ mol^{-1}, which is very close to the experimental value (21.9 kJ mol^{-1}), and closer than previous computational attempts,11–12 which presumably can be largely attributed to the introduction of electron correlation in the calculation. It should also be remembered that this average value refers to urea molecules in a periodic environment; the interactions will be strengthened due to resonance-enhanced bond cooperativity. As mentioned above, ab initio MO calculations for the urea dimer structure (i.e., without resonance enhancement, and just for interaction N-H···O(2), Figure 3a) give a value of about 15 kJ mol^{-1} after Counterpoise correction.18

The primary aim of our calculations was to determine the strengths of the two different interactions, *r*N-H···O(1) and *r*N-H···O(2), rather than just the average value. Accordingly, two further models were subjected to calculation: in the first, one molecule was removed from the unit cell, thus deleting a chain of urea molecules from the crystal lattice, destroying contact *r*N-H···O(1) but retaining *r*N-H···O(2), and in the second lattice parameter "*c*" was stretched from 4.6 to 9.0 Å (to destroy contact *r*N-H···O(2), Figure 3b and c). The results from these calculations are given in Table 3. From this, some interesting geometrical features can be monitored as hydrogen bonds are formed. Model B is fictitious, and as such cannot be substantiated by experiment. Model C, however, is to all intents and purposes the same as the supercell calculation (but with a planar (C_{2v}), rather than puckered (C_2) geometry), which has already been shown above to reproduce the gas-phase experimental geometry to within 0.01 Å. The changes in the molecular structure of urea upon hydrogen bond formation can be summarised as follows: *r*C—O and *r*N—H both lengthen (by about 0.04 and 0.01 Å, respectively), and *r*C—N shortens (by about 0.02 Å). These observations are entirely consistent with resonance-enhanced bond cooperativity. The carbonyl group donates electron density to the hydrogen bonds (thus lengthening them), and *r*N—H will lengthen as the proton is drawn into the hydrogen bond potential well. Finally, *r*C—N will shorten as the nitrogen lone pair is attracted towards the electron-diminished carbon centre.

Table 3. Calculation results for urea models B and C (see Figure 3b, c and text).

Parameters	**Model B**	**Model C**
	(relaxed)	**(relaxed)**
Lattice [Å, °]		
a=*b*	5.604	5.604
c	4.689	9.000
α, β, γ	90.0	90.0
Z	1	1
Volume [Å^3]	147.1	282.6
Point group	C_{2v}	C_{2v}
Geometry [Å]		
*r*C-O	1.251	1.228
*r*C-N	1.352	1.367
*r*N-H(1); *r*N-H(2)	1.013; 1.025	1.013
*r*N-H···O(1)	–	–
*r*N-H···O(2)	2.021	–
Energy		
Total energy [eV]	−1204.007852	−1203.510237
*r*N-H···O(1)	16.5	–
[kJ mol^{-1} per bond][a]		
*r*N-H···O(2)	–	24.0
[kJ mol^{-1} per bond][b]		

[a] $\Delta E[r\text{N-H}\cdots\text{O(1)}]=(E_{solid}/Z-E_{model\ B})/2$. [b] $\Delta E[r\text{N-H}\cdots\text{O(2)}]= (E_{model\ B}-E_{model\ C})/2$.

Comparing the energies obtained for models B and C with that of the optimised cell allows the strengths of the two hydrogen bonds to be obtained. Thus breaking first the interaction N-H···O(1) costs 16.5 kJ mol^{-1} and then breaking N-H···O(2) costs a further 24.0 kJ mol^{-1}. These numbers compare very favourably with those obtained from the experimental/theoretical study detailed above (15.7 and 28.2 kJ mol^{-1}, respectively).16 Therefore, although N-H···O(1) is the shorter of the two interactions, it is also the weaker; this may appear surprising to a first approximation. However, it should be remembered that hydrogen bonds in the solid state are practically never in their optimal geometry, and are always influenced by their surrounding environment.1 This highlights another reason why hydrogen bond energies obtained by the ab initio MO theory route of

isolated-dimer models should be used with caution when used to develop an understanding of properties of the solid state.

Conclusion

In this paper we have demonstrated the use of plane-wave density functional theory to calculate the strengths of hydrogen bonds in periodic lattices. For ammonia, we have been able to reproduce the experimental lattice energy to within 1 kJ mol^{-1}, which allowed us to determine the strength of the trifurcated bond in the crystal structure. This has been shown to be very similar to that of the standard hydrogen bond present in gas-phase ammonia dimers. For urea, we were able to calculate individual values for the two different hydrogen bonds present in the periodic crystal lattice from a purely theoretical study for the first time, and show that the shorter bond is actually the weaker of the two interactions.

Computational Methods

Crystal lattice calculations

Total energy density functional theory calculations have been carried out on the phase I crystal structures of ammonia and urea by using the CASTEP package available through the Materials Studio suite of software.4 Periodic boundary conditions allow the valence electronic wave function to be expanded in terms of a discrete plane-wave basis set, which can be continuously improved until a desired convergence level is reached. The basis sets expressed at cut-offs 550 eV (for ammonia) and 600 eV (for urea) converged the total energies to better than 2.0 meV per unit cell. The electronic core wave function was described by using the standard ultrasoft pseudopotentials available with the software package. Bloch's theorem allows the calculation to run in reciprocal space (i.e., *k*-space); this significantly improves calculation efficiency. The symmetry-reduced *k*-point sets used to sample the reciprocal space were generated by using Monkhurst–Pack grids26 (dimensions 6×6×6, giving 11 *k*-points in the symmetry-reduced first Brillouin zone for ammonia and 4×4×4, giving 6 *k*-points, for urea). The Fast Fourier Transformation (FFT) grid used to communicate between real and reciprocal space was set at 25 % in excess of levels prescribed by the program in order to minimise wrap-around errors in the transformation. The GGA functionals PW9127 and PBE28 were used to model electronic exchange and correlation for ammonia and urea, respectively.

For ammonia, the initial structure was taken from an X-ray diffraction structure determination by Boese et al.8b for the phase I, ambient-pressure cubic crystal system. Optimisation of atomic positions and unit cell parameters were performed on alternate cycles by using the BFGS method until the convergence criteria were met (maximum energy change per atom=5×10^{-6} eV, maximum root-mean-square force=0.01 eV $Å^{-1}$,

maximum RMS stress=0.02 GPa and maximum RMS displacement=5.0×10^{-4} Å). For urea, the starting coordinates and unit cell dimensions were taken from a low-temperature (12 K), ambient-pressure neutron diffraction structure by Swaminathan et al.10 Optimisation was performed in the same fashion as for ammonia until convergence was achieved (maximum energy change per atom=2×10^{-5} eV, maximum RMS force=0.05 eV $Å^{-1}$, maximum RMS stress=0.1 GPa and maximum RMS displacement=2.0×10^{-3} Å).

Supercell calculations

Supercell calculations were performed on single, isolated molecules of ammonia and urea (effectively the gas phase) for comparison with the energy per molecule in the solid state, and thus allowing the deduction of the total intermolecular interaction energies in the two crystal structures. Zero interaction between the nearest neighbouring cells was obtained by increasing the cell size and observing the change in total energy. Cell sizes of 8×8×8 $Å^3$ for ammonia and 10×10×10 $Å^3$ for urea were found to break all intermolecular interactions, without giving rise to overly long computational times. The basis set cut-off energies used previously (550 and 600 eV) were sufficiently high to avoid lowering of the total energy due to the increase in the number of plane waves in the basis sets (as the cell volume increases). Thus, the comparison of energies between the supercell and crystal lattice calculations is legitimate; we estimate any error incurred due to inconsistencies in basis sets to be within 0.001–0.003 eV (i.e., 0.1–0.3 kJ mol^{-1}) per hydrogen bond.

Models used to determine the strengths of N-H···O(1) and N-H···O(2) in urea

Given that two different interactions are present in the phase I structure of urea, rather than just determining the total interaction energy by a supercell calculation, we also performed calculations on two other cells in order to be able to determine the interaction energies of the individual hydrogen bonds directly. To this end, two periodic models were constructed: in the first, one molecule was removed from the unit cell, thus deleting one stack of urea molecules from the crystal lattice and destroying the N-H···O(1) contact (Figure 3b). In the second, the lattice parameter "*c*" was stretched to 9 Å, thus ensuring that all N-H···O(2) contacts were broken (Figure 3c). By comparing the energies (per molecule) obtained for these two models with that of the optimised crystal lattice, the hydrogen bond energies were deduced. The same cut-off energy (600 eV) was used as with the crystal lattice and supercell calculation, with very similar *k*-point sampling grids (reduced to 4×4×3 for the stretched lattice).

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[23] In this work we take the hydrogen bond definition from ref. 1 b), namely that the interaction includes contributions from electrostatics (including dipole-dipole interactions), polarisation, charge transfer and van der Waals forces (including dispersion, *i.e.* induced dipole-induced dipole interactions). Our calculated values therefore include all these terms, with the exception of dispersion that is not modelled with the current generation of DFT functionals. Dispersion effects are, in any case, expected to make only very small contributions to the total interaction energies for the two compounds investigated in this study.

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